

CLAIMS

1. Enzyme component system (ECS) as an oxidation and bleaching system for the preparation of special highly selective oxidants, consisting of

- a) system component 1): at least one hydrolase from enzyme classes 3.1, 3.1.1, 3.1.2, 3.1.3, 3.1.4, or 3.1.7 and/or at least one hydrolase from enzyme classes 3.5, 3.5.1, 3.5.2, 3.5.3, 3.5.4, 3.5.5 or 3.5.99,
- b) system component 2): at least one fatty acid, preferably C_6 to C_{28} (saturated, monounsaturated or polyunsaturated),
- c) system component 3): at least one oxidant precursor for reaction with the enzymes,
- d) system component 4): at least one ketone from the group of carbonyl compounds.

2. Enzyme component system according to Claim 1, characterized in that enzymes of class 3.1.1.3: lipases (triacylglycerol lipase, triglyceroacyl hydrolases) are used as system component 1).

3. Enzyme component system according to Claims 1 and 2, characterized in that enzymes of class 3.5.1.4, amidases, and/or class 3.5.5.1, nitrilases, are used as system component 1).

4. Enzyme component system according to Claims 1 and 2, characterized in that the enzymes of class 3.1.1.3 (lipases) are obtained from organisms such as *Candida antarctica*, *Candida rugosa*, *Candida lipolytica*, *Candida cylindraceae*, *Candida spec.*, *Geotrichum candidum*, *Humicola lanuginosa*, *Penicillium cambertii*, *Penicillium roqufortii*, *Aspergillus spec.*, *Mucor javanicus*, *Mucor mehei*, *Rhizopus arrhizus*, *Rhizopus niveus*, *Rhizopus delamar*, *Rhizopus spec.*, *Chromobacterium viscosum*, *Pseudomonas cepacia* and *Pseudomonas spec.* from wheat seedlings or pancreas (pig or other sources).

5. Enzyme component system according to Claims 1 and 3, characterized in that the enzymes of classes 3.5.1.4 and 3.5.5.1 are obtained from organisms such as *Pseudomonas aeruginosa*, *Pseudomonas putida*, *Pseudomonas acidovorax*, *Pseudomonas spec.*, *Aspergillus nidulans*, *Aspergillus spec.*, *Brevibacterium spec.*, *Streptococcus pneumoniae*, *Rhodococcus spec.* and others.

6. Enzyme component system according to Claims 1 through 5, characterized in that it contains enzymes from fungi, bacteria, animals or plants obtained from natural organisms or organisms modified by genetic engineering.

7. Enzyme component system according to Claims 1 through 6, characterized in that modified enzymes, enzyme constituents, prosthetic groups or mimicking substances are used as catalysts.

8. Enzyme component system according to Claims 1 through 7, characterized in that it contains as system component 2) one or more saturated, monounsaturated or polyunsaturated, preferably C_6 to C_{28} fatty acids according to Appendix 1.

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9. Enzyme component system according to Claim 8, characterized in that it contains as system component 2) preferably tetradecanoic acid (myristic acid) and/or dodecanoic acid (lauric acid).

10. Enzyme component system according to Claims 1 through 9, characterized in that it contains as system component 3) at least one oxidant precursor such as peroxide (H_2O_2), an organic peroxide such as 3-chloroperoxybenzoic acid, Mg monoperoxyphthalate, di-tert-butyl peroxide, cumene hydroperoxide, lauroyl peroxide, chloroperoxybenzoic acid, dicumyl hydroperoxide, methyl ethyl ketone peroxide, benzoyl peroxide, diperoxydodecanedioic acid Na salt and others and a per compound such as a perborate, persulfate, percarbonate, perphosphate, percarbamide, perchlorate etc.

11. Enzyme component system according to Claims 1 and 10, characterized in that it contains as system component 3) the H_2O_2 -activating ions Mo^{6+} , W^{6+} , Va^{5+} and/or compounds such as the nitrilamines and/or dicyandiamides.

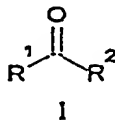
12. Enzyme component system according to Claims 1, 10 and 11, characterized in that it preferably contains H_2O_2 as system component 3).

13. Enzyme component system according to Claims 1, 10 and 11, characterized in that it contains as system component 3) H_2O_2 generated in situ from glucose and GOD.

14. Enzyme component system according to Claims 10 through 13, characterized in that it contains as system component 3) besides per acids also a bleaching activator such as TAED (tetra-acetythylenediamine), TAGU (tetraacetyl glycoluril) and iso-NOBS (sodium p-isononanoyloxy-benzenesulfonate).

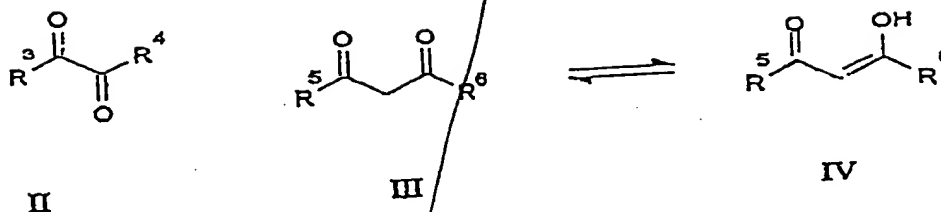
15. Enzyme component system according to Claims 1 and 10 through 14, characterized in that it contains as system component 3) besides the peroxides and/or per compounds also air or oxygen at atmospheric pressure at a slightly positive pressure of up to 2 bar.

16. Enzyme component system according to Claims 1 through 15, characterized in that it contains as system component 4) at least one ketone of general formula I:



wherein the R^1 and R^2 groups are equal or different and denote aliphatic or aromatic groups and furthermore can form a ring containing besides carbon also heteroatoms, such as nitrogen, oxygen and sulfur.

17. Enzyme component system according to Claims 1 through 16, characterized in that it contains as system component 4) a 1,2-diketone of formula II, a 1,3-diketone of formula III or a polyketone (polyketide) as well as a tautomeric enol of formula IV



wherein groups R^3 to R^6 , once again, are equal or different and denote aliphatic or aromatic groups and furthermore groups R^3 and R^4 and groups R^5 and R^6 , together, can form a ring containing besides carbon also heteroatoms such as nitrogen, oxygen or sulfur.

18. Enzyme component system according to Claims 1 through 17, characterized in that it contains as system component 4) besides a general carbonyl compound also a ketone such as, in general, a hydroxyketone, α,β -unsaturated ketone, oxydicarboxylic acid, quinone and halogenated ketone.

19. Enzyme component system according to Claims 1 through 18, characterized in that it contains as system component 4) a compound such as those listed in Appendix 2.

20. Enzyme component system according to Claims 1 through 19, characterized in that it contains a polymerization catalyst such as, in particular, a phenolic substance or polycyclic compound with several oxidizable hydroxyl groups according to Appendix 3.

21. Enzyme component system according to Claims 1 through 20, characterized in that it is possible to add to it as an additional system an enzymatic oxidation system with enzyme action-enhancing compounds, said system containing

- a) at least one suitable oxidation catalyst
- b) at least one suitable oxidant
- c) at least one mediator selected from the group consisting of hydroxylamines, hydroxylamine derivatives, hydroxamic acids, hydroxamic acid derivatives, aliphatic, cycloaliphatic, heterocyclic or aromatic compounds containing at least one N-hydroxy, oxime, N-oxy or N,N'-dioxy function and/or at least one mediator from the group of amides, such as, for example, hydrazides or 1,2,4-triazolidin-3,5-diones (urazoles) and/or at least one mediator from the group of imides such as, for example, the hydantoins, and/or at least one mediator from the group of oxocarbons.

22. Enzyme component system according to Claims 1 through 21, characterized in that it is possible to add to it as an additional system an enzymatic oxidation system with enzyme action-enhancing compounds, said system containing:

at least one mediation enhancer selected from the group consisting of carbonyl compounds, aliphatic ethers, phenol ethers or olefins (alkenes) and/or at least one mediation enhancer selected from the group consisting of NO-, NOH- and HRN-OH compounds and/or amides such as hydrazides or urazoles and/or imides such as hydantoins and/or oxocarbons.

23. Enzyme component system according to Claims 1 through 22, characterized in that it is possible to add to it as an additional system an enzymatic oxidation system with enzyme action-enhancing compounds, said system containing:

at least one mediation enhancer selected from the group consisting of cation radical-generating substances, of the phenothiazine and/or phenoxazine type and/or of the (R=N-N=R) type¹⁰ (for example, ABTS) or of aryl-substituted alcohols (nonphenols) such as, for example, veratryl alcohol and/or phenol derivatives, such as p-hydroxycinnamic acid, 2,4-dichlorophenol, p-hydroxybenzenesulfonate, vanillin (4-hydroxy-3-methoxybenzaldehyde), p-hydroxybenzoic acid, 5-amino-2-hydroxybenzoic acid (5-aminosalicylic acid) and/or Wurster-type radical cation compounds, such as p-phenylenediamine, preferably N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, N,N,N',N'-tetramethyl-p-phenylenediamine, 2,3,5,6-tetramethyl-p-phenylenediamine and/or radical anions, for example semiquinones, which can be generated by enzymatic oxidation of hydroquinones.

24. Enzyme component system according to Claims 1 through 21, characterized in that it is possible to use as oxidation catalysts enzymes such as the oxidoreductases of classes 1.1.1. to 1.97, and preferably:

cellobiose: oxygen-1-oxidoreductase (cellobiose oxidase) (1.1.3.25),
cellobiose: quinone-1-oxidoreductase (1.1.5.1), bilirubin oxidase (1.3.3.5),
cytochrome oxidase (1.9.3), oxygenases, lipoxygenases (1.13, 1.14),
superoxide dismutase (1.15.11), ferrioxdase, for example ceruloplasmin (1.16.3.1),
1.10 such as catechol oxidase (tyrosinase) (1.10.3.1), L-ascorbate oxidase (1.10.3.3), O-aminophenol oxidase (1.10.3.4) and laccase (benzodioxigen oxidoreductase) (1.10.3.2)
1.11 such as cytochrome C peroxidase (1.11.1.5), catalase (1.11.1.6), peroxidase (1.11.1.7), iodide peroxidase (1.11.1.8), glutathione peroxidase (1.11.1.9), chloride peroxidase (1.11.1.10) and L-ascorbate peroxidase (1.11.1.11), phospholipid hydroperoxide glutathione peroxidase (1.11.1.12), manganese peroxidase (1.11.1.13) and diarylpropane peroxidase (ligninase, lignin peroxidase) (1.11.1.14).

25. Enzyme component system according to Claims 1, 21 and 24, characterized in that enzymes such as laccases and/or peroxidases are preferably used as oxidation catalysts.

26. Enzyme component system according to Claim 25, characterized in that it preferably contains laccases and/or peroxidases from white rotting fungi such as, for example, Trametes versicolor, Trametes spec., Phlebia spec., Pleurotus spec., Phanerochaete chrysosporium, Agaricus spec. etc and also other fungi, bacteria, plant and animal cells obtained from natural organisms or organisms modified by genetic engineering.

27. Enzyme component system according to Claims 1, 21 to 26, characterized in that modified enzymes, enzyme constituents, prosthetic groups or mimicking substances are used as the enzyme catalysts.

¹⁰ N means nitrogen, R denotes groups.

28. Enzyme component system according to Claims 21 through 27, characterized in that it employs as additional oxidants preferably air, oxygen, ozone, a peroxide such as H_2O_2 , an organic peroxide, a per acid such as peracetic, performic, persulfuric, pernitric, metachloroperoxybenzoic and perchloric acid, a per compound such as a perborate, percarbonate and persulfate, or oxygen species and the radicals thereof such as the OH, OOH and OH^\cdot radical, superoxide (O_2^\cdot), dioxygenyl cation (O_2^+), singlet oxygen, ozonide (O_3^\cdot), dioxiranes, dioxitanes or Fremy radicals.
29. Enzyme component system according to Claims 21 through 28, characterized in that the mediators and additional mediation enhancers are those shown in Appendix IV and IVa.
30. Enzyme component system according to Claims 21 through 29, characterized in that the mediator/mediation enhancer ratio is from 5000:1 to 5:1 and preferably from 500:1 to 5:1.
31. Use of the enzyme component system according to Claims 1 to 30 in a process for the delignification and/or modification and/or bleaching of cellulose from wood or annual plants and of wood pulps and deinked pulps, whereby the reaction of the enzyme component system is carried out at a pH from 2 to 11, preferably at pH 3 to 9, at a temperature from 20 to 95 °C, preferably from 40 to 95 °C, at a pulp consistency from 0.5 to 40%, preferably from 4 to 15%, in the presence of oxygen or air at atmospheric pressure or a slightly positive pressure (up to 2 bar), and system component 1, namely lipase from *Humicola lanuginosa*, is used at a concentration from 0.05 to 5 mg, preferably from 0.05 to 2 mg, and amidase from *Pseudomonas aeruginosa* is used at a concentration from 40 to 200 IU, and system component 2, namely one or more fatty acids, preferably C_8 to C_{18} fatty acids, preferably tetradecanoic and/or dodecanoic acid, are used at a concentration from 0.05 to 20 mg, preferably from 0.05 to 10 mg, and system component 3, namely the oxidant precursor, preferably H_2O_2 , is used at a concentration from 0.05 to 20 mg (100%), preferably from 0.05 to 10 mg, and system component 4, namely a ketone, preferably benzophenone, is used at a concentration from 0.05 to 20 mg, preferably at a concentration from 0.05 to 10 mg, in each case based on 1 g of absolutely dry pulp.
32. Use of the enzyme component system according to Claims 1 and 31 in a process for the delignification and/or modification and/or bleaching of cellulose from wood or annual plants and of wood pulps and deinked pulps, whereby an acid wash or a Q-step is used before and/or after the reaction of the enzyme component system and the acid wash is carried out at 60-120 °C, at pH 2 to 5.5, for 30-90 min and at 4-20% pulp consistency, and the Q-step is carried out with 0.05-1%, preferably with 0.2 to 0.5% of chelator at 60-100 °C, at pH 2 to 5.5 for 30-90 min and at a pulp consistency of 4-20%.
33. Use of the enzyme component system according to Claims 1, 31 and 32 in a process for the delignification and/or modification and/or bleaching of cellulose from wood or annual plants and of wood pulps and deinked pulps, whereby the acid wash and the Q-step are carried out for 1 hour at 60-90 °C, at pH 2 to 5 and at 10% pulp consistency.

34. Use of the enzyme component system according to Claims 1, 31 to 33 in a process for the delignification and/or modification and/or bleaching of cellulose from wood or annual plants and of wood pulps and deinked pulps, whereby said system can be used before or after any possible treatment of the pulp by single or multiple digestion, bleaching steps or other pre- and post-treatments, such as alkaline leaching, alkaline extraction, washing, acid treatment, Q-step, O₂ delignification step, peroxide bleaching step, O₂-promoted peroxide step, pressure peroxide step, per acid step, per acid-promoted O₂ or peroxide step, ozone bleaching step, dioxirane step, polymethoxalate step, Cl-delignification step, ClO₂ bleaching step, Cl/ClO₂ bleaching step, reductive bleaching steps, sulfonation steps, NO/NO₂ treatments, nitrosylsulfuric acid treatment, swelling steps, enzyme treatments, for example treatments with hydrolases such as cellulases and/or hemicellulases (for example, xylanase, mannanase, etc) and/or pectinases and/or proteinases and/or lipases and/or amidases and/or oxidoreductases, such as, for example, laccases and/or peroxidases etc or several combined treatments.

35. Use of the enzyme component system according to Claims 1 and 34 in a process for the delignification and/or modification and/or bleaching of cellulose from wood or annual plants and wood pulps and deinked pulps, whereby the swelling step is carried out with the aid of substances such as, for example, glycols, such as propylene glycol or ethylene glycol, glycol ethers such as ethylene glycol dimethyl ether etc, but also with the aid of solvents, for example, alcohols such as methanol, ethanol, butanol, amyl alcohol, cyclohexanol, benzyl alcohol and chlorohydrin, phenols such as phenol, methylphenols and methoxyphenols, aldehydes such as formaldehyde and chloral, mercaptans such as butyl mercaptan, benzyl mercaptan and thioglycolic acid, organic acids such as formic, acetic and chloroacetic acid, amines such as ammonia and hydrazine, hydrotropic solvents, for example a concentrated solution of sodium benzoate, other substances such as benzenes, pyridines, dioxane, ethyl acetate, and other basic solvents such as OH/H₂ or OH/alcohol etc.

36. Use of the enzyme component system according to Claims 1 to 35 in a process for the delignification and/or modification and/or bleaching of cellulose from wood or annual plants and of wood pulps and deinked pulps, whereby there is added to the reaction solution a complexing agent such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylenediaminetetraacetic acid (HEDTA), diethylenetriaminopentamethylenephosphonic acid (DTMPA), nitrilotriacetic acid (NTA), polyphosphoric acid (PPA) or other complexing agents for iron, manganese or copper, for example diethylamine or hydroxylamine.

37. Use of the enzyme component system according to Claims 1 to 36 in a process for the delignification and/or modification and/or bleaching of cellulose from wood or annual plants and of wood pulps and deinked pulps, said process being carried out in several steps and whereby between each step is applied a washing or washing and extraction step with alkaline hydroxide solution, or neither washing nor extraction takes place.

38. Use of the enzyme component system according to Claims 1 to 37 in the treatment of paper production wastewater (grinder wastewater, TMP wastewater) and of wastewater from other branches of the industry, such as wood pulp wastewater and textile production wastewater, among others, whereby the reaction of the enzyme component system is carried out at pH 2 to 11, preferably 3 to

6, at a temperature from 20 to 95 °C, preferably from 40 to 95 °C, in the presence of oxygen or air at atmospheric pressure or slightly positive O₂ pressure (up to 2 bar), and system component 1, namely lipase from *Aspergillus spec.* is used at a concentration from 0.05 to 50 mg, preferably from 0.5 to 10 mg, and system component 2, namely one or more fatty acids, preferably C₈ to C₁₈ fatty acids, preferably tetradecanoic acid and/or dodecanoic acid, is used at a concentration from 0.05 to 200 mg, preferably at a concentration from 0.05 to 50 mg, and system component 3, namely the oxidant precursor, preferably H₂O₂, is used at a concentration from 0.05 to 200 mg (100%), preferably at a concentration from 0.05 to 50 mg, and system component 4, namely a ketone, preferably a benzophenone, is used at a concentration from 0.05 to 200 mg, preferably at a concentration from 0.05 to 50 mg, and that a polymerization catalyst, preferably purpurogallin, is used at a concentration from 0.005 to 200 mg, preferably at a concentration from 0.005 to 50 mg, the concentrations in all cases being based on 1 liter of wastewater.

39. Use of the enzyme component system according to Claims 1 to 38 for the production of lignin solutions or gels and of the corresponding binders/adhesives, and for the production of wood-based composites, whereby the reaction of the enzyme component system is carried out at pH 2 to 11, preferably 3 to 6, at a temperature from 20 to 95 °C, preferably from 40 to 95 °C, in the presence of oxygen or air at atmospheric pressure or slightly positive O₂ pressure (up to 2 bar), and system component 1, namely lipase from *Humicola lanuginosa* is used at a concentration from 0.05 to 50 mg, preferably from 0.5 to 10 mg, and system component 2, namely one or more fatty acids, preferably C₈ to C₁₈ fatty acids, preferably tetradecanoic acid and/or dodecanoic acid, is used at a concentration from 0.05 to 200 mg, preferably at a concentration from 0.05 to 50 mg, and system component 3, namely the oxidant precursor, preferably H₂O₂, is used at a concentration from 0.05 to 200 mg (100%), preferably at a concentration from 0.05 to 50 mg, and system component 4, namely a ketone, preferably a benzophenone, is used at a concentration from 0.05 to 200 mg, preferably at a concentration from 0.05 to 50 mg, and that a polymerization catalyst, preferably purpurogallin, is used at a concentration from 0.005 to 200 mg, preferably at a concentration from 0.005 to 50 mg, the concentrations in all cases being based on 1 liter of wastewater.

40. Use of the enzyme component system according to Claims 1 to 39 in a process for the enzymatic printing ink removal during the deinking of waste paper, whereby the reaction of the enzyme component system is carried out at pH 7 to 11, preferably at pH 7 to 9, at a temperature from 20 to 95 °C, preferably from 40 to 95 °C, in the presence of oxygen or air at atmospheric pressure or slightly positive O₂ pressure (up to 2 bar), and system component 1, namely lipase from *Humicola lanuginosa*, is used at a concentration from 5 to 500 mg, preferably from 5 to 100 mg, and system component 2, namely one or more fatty acids, preferably C₈ to C₁₈ fatty acids, preferably tetradecanoic acid and/or dodecanoic acid, is used at a concentration from 5 to 2000 mg, preferably at a concentration from 5 to 500 mg, and system component 3, namely the oxidant precursor, preferably H₂O₂, is used at a concentration from 5 to 5000 mg (100%), preferably at a concentration from 5 to 1000 mg, and system component 4, namely a ketone, preferably a benzophenone, is used at a concentration from 5 to 2000 mg, preferably at a concentration from 5 to 500 mg, and that, to change the optimum pH for the printing ink removal reaction and to affect the swelling behavior of the waste paper, a phenolic or polycyclic substance with several oxidizable hydroxyl groups, preferably bisphenol

46. Use of the enzyme component system according to Claims 1 to 45 in a process for the enzymatic liquefaction of coal, whereby the reaction of the enzyme component system is carried out at a pH from 2 to 11, preferably at pH 3 to 9, at a temperature from 20 to 95 °C, preferably from 40 to 95 °C, at a coal slurry consistency from 0.5 to 40%, preferably from 4 to 15%, in the presence

of oxygen or air at atmospheric pressure or a slightly positive O₂ pressure (up to 2 bar), and system component 1, namely lipase from *Humicola lanuginosa* is used at a concentration from 0.05 to 20 mg, preferably from 0.05 to 10 mg, and system component 2, namely one or more fatty acids, preferably C₈ to C₁₈ fatty acids, preferably tetradecanoic and/or dodecanoic acid, is used at a concentration from 0.05 to 100 mg, preferably from 0.05 to 50 mg, and system component 3, namely the oxidant precursor, preferably H₂O₂, is used at a concentration from 0.05 to 50 mg (100%), preferably from 0.05 to 50 mg, and system component 4, namely a ketone, preferably a benzophenone, is used at a concentration from 0.05 to 100 mg, preferably at a concentration from 0.05 to 50 mg, in each case based on 1 g of coal (lignite).

47. Use of the enzyme component system according to Claims 1 to 46 in a process for detergent bleaching, whereby the reaction of the enzyme component system is carried out at a pH from 2 to 12, preferably at pH 3 to 10, at a temperature from 20 to 95 °C, preferably from 30 to 95 °C, in the presence of oxygen or air at atmospheric pressure or at a slightly positive O₂ pressure (up to 2 bar), and system component 1, namely lipase from *Humicola lanuginosa*, is used at a concentration from 0.05 to 20 mg, preferably from 0.05 to 10 mg, and system component 2, namely one or more fatty acids, preferably C₈ to C₁₈ fatty acids, preferably tetradecanoic and/or dodecanoic acid, is used at a concentration from 0.05 to 50 mg, preferably at a concentration from 0.05 to 20 mg, and system component 3, namely the oxidant precursor, preferably H₂O₂, is used at a concentration from 0.05 to 50 mg (100%), preferably at a concentration from 0.05 to 20 mg, and system component 4, namely a ketone, preferably a benzophenone, is used at a concentration from 0.05 to 50 mg, preferably at a concentration from 0.05 to 20 mg, in each case based on 100 mL of washing solution.

48. Use of the enzyme component system according to Claims 1 to 47 in a process for detergent bleaching, whereby the system is added to a detergent formulation with all its technically common and known deterative substances or detergent additives.

49. Use of the enzyme component system according to Claims 1 to 48 in a process for bleaching and/or decolorizing textile fabrics, whereby the reaction of the enzyme component system is carried out at a pH from 2 to 11, preferably at pH 3 to 9, at a temperature from 20 to 95 °C, preferably from 40 to 95 °C, at a fabric density from 0.5 to 40% and preferably from 4 to 15%, in the presence of oxygen or air at atmospheric pressure or at a slightly positive O₂ pressure (up to 2 bar), and system component 1, namely lipase from *Humicola lanuginosa* is used at a concentration from 0.05 to 10 mg, preferably from 0.05 to 5 mg, and system component 2, namely one or more fatty acids, preferably C₈ to C₁₈ fatty acids, preferably tetradecanoic and/or dodecanoic acid, is used at a concentration from 0.05 to 20 mg, preferably from 0.05 to 10 mg, and system component 3, namely the oxidant precursor, preferably H₂O₂, is used at a concentration from 0.05 to 20 mg (100%), preferably at a concentration from 0.05 to 10 mg, and system component 4, namely a ketone, preferably a benzophenone, is used at a concentration from 0.05 to 20 mg, preferably at a concentration from 0.05 to 10 mg, in each case based on 1 g of denim.

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A₁

add
B₁

add
C₁

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